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The universe of operations of thermodynamics vis-à-vis Boltzmann integro-differential equation†

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Abstract : In a previous paper [*Indian J. Phys.* **76B** 715 (2002)], we have elaborated Bridgman's assertion about the "universe of operations" of thermodynamics which revealed that the time scale shorter than τ_{therm} (the minimum time required for sensing of thermal interaction) falls in the domain of natural fluctuations. Using the Boltzmann integro-differential equation, we have traced in this paper, the origin of the natural fluctuations which in essence, is the case of breakdown of the *equal a priori probability* for binary collisions and their reverse ones. Thus the natural fluctuations about equilibrium states (both under adiabatic and non-adiabatic conditions), nonequilibrium stationary states and the general nonequilibrium states have been discussed. Using the deductions thereof, the mathematical expressions for probability of achieving nonequilibrium state on account of natural fluctuations about equilibrium and nonequilibrium states have been rationalized These deductions also help in understanding the origin of replicas of a given system in a Gibbsian ensemble. These findings are crucial for developing an irreversible thermodynamic framework and also for evolving corresponding statistical mechanical description. The minimum time scale of τ_{therm} when imposed on the statistical mechanical description, generates the corresponding thermodynamic description and hence the application of this condition is indeed, an act of imposing the dictates of the laws of thermodynamics on the microscopic level of mathematical expressions.

Keywords : Statistical mechanics, irreversibility, fluctuations, nonequilibrium thermodynamics, Gibbsian ensemble.

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1. Introduction

In a previous paper [1], we have discussed the details of Bridgman's assertion [2] that the universe of operations of thermodynamics is determined by the 'instrumental operations of laboratory" otherwise it would be a mere "paper and pencil operation' and that of Eddington's law of Nature [3] that "time's arrow is the property of entropy alone'. On the other hand, one also has a notion that a thermodynamical description needs to be based on the laws of thermodynamics [1, 4-9] and hence, it should conform to the above stated Bridgman's assertion. On investigating this aspect [1], it gets revealed that the minimum time required for sensing the thermal interaction, $\tau_{therm}(>>\tau_{fluc}$, the time scale of the natural fluctuational processes), determines the lower limit of time scale amenable to thermodynamics as it is inherent in the laws of thermodynamics, which is the precise meaning of Bridgman's said assertion. It then implies that τ_{therm} is the minimum length of time's arrow (the property inherent in all irreversible processes), as the unidirectionality is non-existent in the natural fluctuational processes. Thus in all time rates encountered in thermodynamics (irreversible), the infinitesimal time interval dt is limited as $dt \geq \tau_{therm}$ and precisely herein lies the crux of Eddington's law of Nature. Moreover, on realizing that as the time scale $\tau \geq \tau_{therm}$ is inherent in the laws of thermodynamics and hence that in the thermodynamic principle based on the second law, namely, for an adiabatically closed system, the entropy is never a decreasing function, one is led to Eddington's law of Nature. The rigour of these revelations is that one should not use the thermodynamic framework for processes whose time scales are less than τ_{therm} and hence it conforms well to the standard thermodynamic assertion that the time scales of τ_{fluc} remain out side of the scope of thermodynamics. We have also shown therein [1] that the

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thermodynamic irreversibility is all about the imbalances in the chemical interactions and the latter has additional facets over and above the traditionally known ones namely the chemical reactions and the matter diffusion.

As the above stated deductions are based on the macroscopic level of considerations, it now becomes imperative to throw further light on some of them from microscopic point of view. Therefore in this paper, we are using the Boltzmann integro-differential equation as applied to non-uniform monatomic gases and trace the origin of the *natural fluctuations*. The results of this exercise also help in clarifying the state of art of the Gibbsian ensemble method that is used in statistical mechanics vis-à-vis irreversible thermodynamics, statistical thermodynamics and nonequilibrium statistical mechanics [10-13].

2. Boltzmann integro-differential equation revisited

Let us consider for the sake of simplicity, a non-uniform monatomic ideal gas and assume that the body forces either do not exist or contribute insignificantly. The Boltzmann integro-differential equation in this case reads as [14-19]

$$\frac{\partial f}{\partial t} + v.\frac{\partial f}{\partial r} = J(f|f), \tag{1}$$

where f is the distribution function of molecules with chaotic velocity C between C and $C + dC$ at the position vector r between r and $r + dr$, v is the molecular velocity and $J(f|f)$ is the collisional integral that reads as [15]

$$J(f|f) = \iint \sigma \, d\Omega \, g \, dv \left(f' \tilde{f}' - f \tilde{f} \right), \tag{2}$$

where σ is the scattering cross section, $d\Omega$ is the differential element of the solid angle, $f, \tilde{f}, f'$ and $\tilde{f}'$, are the distribution functions before (the unprimed ones) and after (the primed ones) a binary collision and g is the relative speed just before the collision, namely :

$$g = |v - \tilde{v}| \tag{3}$$

To save the space, we are not giving the details of the step-by-step derivation of eq.(2) but it is a standard one and the reader may refer any one of the standard texts cited herein [10, 12, 14-21].

Now recall that our previous elucidation [1] has revealed that τ_{therm} is much larger than τ_{flur}, however, to comprehend it from molecular level events we take the help of an earlier elaboration by Balescu [20], wherein he states that there exists a time interval dt having two properties :

(a) dt is much longer than the duration of a collision, τ_c, that is, the time necessary to turn the initial vector g into the final vector $g\varepsilon$, where ε is the unit vector in the direction of the relative velocity of the molecules just after the collision.

(b) dt is much shorter than the relaxation time, τ_r, that is the time it takes for the distribution function (at fixed r and v) to change its value appreciably.

In the light of the above elaboration, it is easy to comprehend that the minimum length of the time duration dt of eq. (1) is determined by $dt \approx \tau_{therm} << \tau_r$.

In kinetic theory, the per unit mass entropy s is defined as [14-19]

$$\rho s = -k_B \int f(\ln f - 1)\, dv, \tag{4}$$

where ρ is the mass density and k_B is the Boltzmann constant, the entropy balance equation is obtained as

$$\rho \frac{ds}{dt} + div\, J_s = \sigma_s \tag{5}$$

with the following expressions for the entropy flux density J_s and the entropy source strength σ_s, namely :

$$J_s = -k_B \int C(\ln f - 1)\, f\, dv, \tag{6}$$

$$\sigma_s = -k_B \int J(f|f) \ln f \, dv, \tag{7}$$

and the chaotic velocity C is given by,

$$C = v - u \tag{8}$$

where u is the barycentric velocity.

The traditional demonstration of the positive definite sign of σ_s (see for example, Ref. [21]) uses the fact that the integrand of eq. (7) by a simple algebra can be manipulated as

$$\sigma_s \propto -J(f+f)\ln f = -\frac{1}{4} J(f+f) \ln\left(\frac{f\tilde{f}}{f'\tilde{f}'}\right) \geq 0 \tag{9}$$

as $J(f|f)$ in its integrand contains the term $\left(f'\tilde{f}' - f\tilde{f}\right)$ (cf. eq. (2)). Hence, $\left(f'\tilde{f}' - f\tilde{f}\right)\ln\left(f\tilde{f}/f'\tilde{f}'\right)$, the negative definite quantity, determines the sign of σ_s. Therefore, it is taken as the statistical mechanical counter-part of the second law of thermodynamics [21], which in other words means that eq. (5) indeed is the Clausius – Duhem inequality, namely :

$$\rho \frac{ds}{dt} + div\, J_s = \sigma_s \geq 0, \tag{10}$$

the local level requirement based on the second law of thermodynamics [22, 23].

This amazingly simple but a powerful demonstration however rests on the assumption of '*equal a priori probability*' of all forward and their reverse collisions. The said assumption of

equal a priori probability' works only because the dt of eq. (1) equals the above stated time scale of τ_{therm}, the minimum time required for sensing of thermal interaction. At the molecular level, it means that during τ_{therm}, all molecules contained in the volume element dr have undergone at least one collision. It is pertinent to recall Tolman's way of description [10], namely, $f'\tilde{f}'\ln\left(f\tilde{f}/f'\tilde{f}'\right)$ is the contribution to σ_s due to the said reverse collisions that is due to the entering of the molecules into the velocity slices of f and $\tilde{f}$ originally belonging to the velocity slices of f' and $\tilde{f}'$. Similarly, $f\tilde{f}\ln\left(f\tilde{f}/f'\tilde{f}'\right)$ is the contribution to σ_s due to the collisions of molecules that leave the velocity slices of f and $\tilde{f}$ and enter into the velocity slices of f' and $\tilde{f}'$. Thus as all binary collisions and their reverse ones have been counted in eq. (1) it means that the constraint of $dt \geq \tau_{therm}$ has been incorporated. The last named condition obviously implies the imposition of the dictates of the laws of thermodynamics on the above microscopic level of description.

3. Origin of natural fluctuations

In order to comprehend the origin of the natural fluctuations from the molecular level events, we recall that the natural fluctuations appear only if the measurements are performed within the time scale less than τ_{therm} [1, 2]; hence it is logical to infer that the said assumption of 'equal a priori probability' breaks down for all-binary collisions or for a few ones that occur within the time interval $dt < \tau_{therm}$. Therefore, eq. (1) counts (on integration) only a part of the number of collisions that occur within the time interval $dt < \tau_{therm}$ and for the collisions not counted by eq. (1) the Boltzmann integro-differential equation obviously would read as [24]

$$\frac{\partial f''}{\partial t} + v.\frac{\partial f''}{dr} = J(f'''), \tag{11}$$

where

$$J(f''') < 0 \text{ for } f''' = f' \tag{12}$$

that is, when one is describing the rate of change of distribution function for either of the two molecules of the colliding pair. However, the same collision also changes the distribution functions of the two molecules of the pair that emerged after the collision. Hence, we have

$$J(f''') > 0 \text{ for } f''' \neq f'', \tag{13}$$

Thus, eq. (12) accounts for the collisions by which the molecules leave the velocity slice to which f'' belongs and eq. (13) counts those collisions by which molecules enter into the velocity slice to which f'' belongs. In view of this, σ_s now has two contributions namely, $\sigma_s(2)$, the one which is traditionally computed as

$$\sigma_s(2) \propto -\frac{1}{4}\left(f'\tilde{f}' - f\tilde{f}\right)\ln\left(\frac{f\tilde{f}}{f'\tilde{f}'}\right) > 0 \tag{14}$$

and the other is $\sigma_s(1)$ which we need to compute by treating those collisions which are devoid of their reverse ones as forward collisions. $\sigma_s(1)$ then reads (in view of Tolman's explanation regarding the molecular collisional contributions to σ_s) as

$$\sigma_s(1) \propto -\frac{1}{4} f''\tilde{f}''\ln\left(\frac{f''\tilde{f}''}{f'''\tilde{f}'''}\right) \gtrless 0. \tag{15}$$

In eq. (15), $f''\tilde{f}''$ is a positive number and hence the sign of $\sigma_s(1)$ is determined by the ratio $\left(f''\tilde{f}''/f'''\tilde{f}'''\right)$ appearing therein. But this ratio could be greater than or less than 1. Thus the sign of eq. (15) may be positive or negative *ie* there is no definite sign of $\sigma_s(1)$. Therefore, the overall entropy source strength σ_s, looses its positive definite character and reads as

$$\sigma_s = \sigma_s(2) + \sigma_s(1) \gtrless 0. \tag{16}$$

However, if one waits for a time period $dt \geq \tau_{therm}$ for an experimental measurement, the reverse collisions will also occur that will contribute a term

$-(1/4)f'''\tilde{f}'''\ln\left(f'''\tilde{f}'''/f''\tilde{f}''\right)$ making $\sigma_s(1)$ as non-existent. By this act, eq. (15) gets transformed to the form of eq. (14). In this latter case, we have

$$\sigma_s \approx \sigma_s(2) > 0 \text{ for } dt \geq \tau_{therm}. \tag{17}$$

From the above discussion, it is clear that as $dt \to \tau_{fluc}$, $\sigma_s(2) \to 0$ and σ_s remains determined only by $\sigma_s(1)$, namely:

$$\sigma_s \approx \sigma_s(1) \gtrless 0 \text{ for } dt \approx \tau_{fluc}. \tag{18}$$

Thus, one is now within the domain of natural fluctuations only.

4. Behaviour of σ_s about an equilibrium state

When a system happens to be in equilibrium, no spatial non-uniformity exits and there is no need to use the local level description. Hence, the Clausius-Duhem inequality [eq. (10)] gives the deDonderian equation [25], namely:

$$\frac{dS}{dt} = \frac{d_e S}{dt} + \frac{d_i S}{dt}, \tag{19}$$

where

$$S = \int \rho s dV, \tag{20}$$

$$\frac{dS}{dt} = \int_V \rho \frac{ds}{dt} dV . \tag{21}$$

Thus when a system is in equilibrium and if it is adiabatically closed $(d_e S / dt = 0)$, then during the time interval $dt(\geq \tau_{therm})$, the second law of thermodynamics demands $d_i S / dt = 0$ and $\sigma_s = 0$ (as σ_s cannot be negative). Now if the measurements are made on such a system within the time intervals $dt \geq \tau_{therm}$, the entropy balance will be determined by

$$\frac{dS}{dt} = \int_V \rho \frac{ds}{dt} dV$$

$$= \int \sigma_s(2) dV + \int \sigma_s(1) dV . \tag{22}$$

(for $dt < \tau_{therm}$)

As $\sigma_s(2)$ is a positive rate, the integral containing it (cf. eq. (22)) primarily drags an adiabatically closed system towards an equilibrium state. However, as the time scale considered herein is of the order of $dt < \tau_{therm}$ and the natural fluctuations considered are those about an equilibrium state, hence, in the majority of binary collisions that occur the distribution function remains collisional invariant. Thereby, the magnitude of $\sigma_s(2)$ (cf. eq. (14)) remains practically very small and comparable to or even less than that of $\sigma_s(1)$. Since $\sigma_s(1)$ has no definite sign and hence the integral containing it (cf. eq. (22)) has no definite sign; however, it may assist $\sigma_s(2)$ or oppose it. This therefore, means that during the time interval $dt < \tau_{therm}$ if $\sigma_s = (\sigma_s(2) + \sigma_s(1)) > 0$, then the adiabatically closed system is on the way towards an equilibrium-state irrespective of whether $\sigma_s(1)$ is positive or negative. If the time period of measurement dt is so short that no worth counting reverse collisions occur, then σ_s and hence $d_i S / dt$ is determined only by $\sigma_s(1)$, and if the latter is a positive quantity then the system is still being dragged towards an equilibrium state. On the other hand, when $\sigma_s = (\sigma_s(2) + \sigma_s(1)) < 0$, the system is necessarily on the way going away from an equilibrium state on account of the natural fluctuations, as $\sigma_s(1)$ is a negative quantity and dominates over σ_s (2), which means that globally dS / dt is negative. Moreover, if the observation is made during a succession of time intervals $dt \approx \tau_{fluc}$, the quantity σ_s (2) remains insignificant because the said reverse collisions do not occur within such a short time interval dt. Thus, the σ_s will be observed as a positive quantity when σ_s (1) incidentally happens to be a positive quantity and the system would be approaching towards an equilibrium state that too solely on account of $\sigma_s(1)$. Whereas, if σ_s is observed as a negative quantity, then the system is being carried away from an equilibrium state again because of the natural fluctuational process as now $\sigma_s(1)$ happens to be a negative quantity. However, it is not possible to guarantee a particular sign sequence and magnitude of $\sigma_s(\approx \sigma_s(1))$ in a succession of measurements in the time intervals of $dt \approx \tau_{fluc}$. So the amplitude of the observed fluctuation in S cannot be uniformly same as the measurements are made for a succession of time intervals $dt \approx \tau_{fluc}$. It is astonishing to learn that even during the natural fluctuations, the second law of thermodynamics has such a strong hold. If it were not so, then the principle of monotonic increase of entropy (for an adiabatically closed system) will not get generated from the microscopic considerations. Further, it is easy to realize that as a system in equilibrium does not have a spatial non-uniformity, the natural fluctuations within an adiabatically closed system cannot generate a spatial non-uniformity because $\sigma_s(1)$ is a scalar quantity which will have a uniformly same magnitude throughout the system.

5. Behaviour of σ_s about a nonequilibrium state

In order to have a maximum level of generality of deductions, let us consider a spatially non-uniform system, which demands to have a discussion at the local level. As demonstrated previously [1], from the thermodynamic point of view, a system can be said to have moved from one nonequilibrium state to another, if it is allowed to interact internally and with its surroundings for time interval $dt \geq \tau_{therm}$. Thus, the sign of dS/dt (cf. eq. (10)) is determined by $(-div J_s + \sigma_s)$. However, if the measurements are carried out for the time intervals $dt < \tau_{therm}$, then we have

$$\rho \frac{ds}{dt} = -div J_s + \sigma_s(2) + \sigma_s(1) . \tag{23}$$

Hence, the succession of measurements for the time interval $dt < \tau_{therm}$ will produce a fluctuating rate of change of S because now $\sigma_s(1)$, the source of natural fluctuations, contributes significantly. Therefore, in this case, the entropy of the system will be found as oscillating (small) about its value for the nonequilibrium state in question. Whereas, if a succession of observations are made for the time intervals $dt \approx \tau_{fluc}$, $\sigma_s(2)$ will be almost equal to zero and the rate of entropy change will be determined by

$$\rho \frac{ds}{dt} = -div J_s + \sigma_s(1)$$

which clearly shows that the observed natural fluctuations will also have a significant contribution from $div J_S$. The above description does hold good for nonequilibrium stationary states too. The only speciality in the latter case is that the average value of $(-div J_s + \sigma_s(2) + \sigma_s(1))$ taken over for a time period $dt \approx \tau_{therm}$, remains identically equal to zero.

6. Probability and σ_s (1)

As said above, σ_s (1) appears only because during a time interval $dt \approx \tau_{therm}$, the equal *a priori* probability for binary collisions and their reverse ones cannot be guaranteed for all collisions that have taken place in this time interval. However, it is not possible to tell forehand which velocity slices would be involved in the binary collisions contributing to σ_s (1) in such a given time interval. This therefore, demands the use of probabilistic approach in this time interval; however, this requirement remains deeply buried in the principle of monotonic increase of entropy for adiabatically closed systems because the working domain of the latter principle is $dt \geq \tau_{therm}$. Of course, one can still perform measurements within the time intervals $dt < \tau_{therm}$ but then creeps-in the need of using the probabilistic approach.

Now recall that when a system is allowed to evolve adiabatically from a given nonequilibrium state, it traverses ($dt \geq \tau_{therm}$) a succession of nonequilibrium states of increasing entropy and finally attains an equilibrium state of maximum entropy. However, as the system evolves the rate of increase of entropy gradually drops. This means that the nonequilibrium states through which the system makes a detour, are occupied for different lengths of time and hence they are the transient states. The mean lifetime of these transient states would be minimum for the farthest away ones from the final equilibrium state. Hence, it is logical that Einstein's formula [26, 27] of the probability P of a nonequilibrium state attained on account of fluctuation about an equilibrium state, reads as

$$P \propto \exp(\Delta S / k_B), \tag{25}$$

where

$$\Delta S = \left(S - S^e\right) < 0. \tag{26}$$

Thus, the small fluctuations have considerably higher probability relative to that for the larger ones. As dt is very small in the natural fluctuational domain, it is guaranteed that σ_s (1) dt in all probability will be much smaller than the magnitude of entropy of the given equilibrium state of a uniform gas.

Similarly, the probability, P, of a fluctuation about a nonequilibrium stationary state and about a general nonequilibrium state will be given by

$$P \propto \exp\left(-|\Delta s| / k_B\right), \tag{27}$$

where Δs is the change in entropy of the system on a natural fluctuation and is given by

$$\Delta s = \left(s - s^{ne}\right) \gtrless 0, \tag{28}$$

$$\Delta s = \left(s - s^{nss}\right) \gtrless 0, \tag{29}$$

where the superscripts *ne* and *nss* stand for the reference nonequilibrium and nonequilibrium stationary states respectively. In this case we have

$$\Delta s \approx \left(-divJ_s + \sigma_s(2) + \sigma_s(1)\right) dt. \tag{30}$$

As dt is very small Δs is guaranteed as very small compared to s^{ne}, s^{nss} and from eq. (27), the relatively small fluctuations have higher probability than that for the relatively larger ones.

7. Construction of an ensemble in the case of equilibrium

The above discussion clarifies that a thermodynamic property of a system needs to be measured on the time scale greater than or equal to τ_{therm}, which is the minimum time required for thermodynamic equilibration of the used measuring gadget with a local pocket of the system. On the other hand, if the efficiency of the measuring gadget is pretty high and the measurement is made in the time scales of τ_{fluc}, it would produce a reading that will most probably have a substantial contribution from natural fluctuations. Thus, all readings taken in the time interval τ_{fluc} when averaged over the time duration of τ_{therm}, will produce a value that will be identical with the one registered in a corresponding single measurement of duration $dt = \tau_{therm}$. Thus, if the property in question is say X, then $\overline{X}$ is the average value of X over the time interval $dt \approx \tau_{therm}$. However, as we have seen above that the natural fluctuation is a statistical phenomena, each measured value $\overline{X}$ for an equilibrium state still may have a very small contribution from the natural fluctuations, that is all contributions from the natural fluctuations may not get exactly counter-balanced. Hence, if the measurements were made in a succession of time intervals τ_{therm} for infinite number of times, there would be observed a very small spread in the value of $\overline{X}$. Therefore, the average of all such measurements $\overline{\overline{X}}$, will correspond to the thermodynamic value of the property for an equilibrium state.

In view of the above, it is easy to realize that each value of $\overline{X}$ corresponds to one particular system of a Gibbsian ensemble [10, 11]. As an equilibrium state of a system is under consideration the corresponding Gibbsian ensemble virtually consists of a infinite number of the replicas of the given system under the given constraints because in principle we can repeat the measurement of a property infinite number of times when a system is in equilibrium. Thus, herein lies the origin of the *ergodic hypothesis* and the assumption used in the ensemble method of statistical mechanics namely "*the (sufficiently long) time average of every physical observable is equal to its ensemble average*" [10, 11, 28-30]. Therefore, $\overline{\overline{X}}$ is not only a time average but also an ensemble average of the thermodynamic property in question. Of course in practice, one is not required to literally take an infinite number of readings (each corresponding to the time duration of τ_{therm}) in order to be

confident of the measured value as a true value of the property. That is, one is allowed to have an ensemble not consisting of a infinite number of systems but for the mathematical convenience an ensemble is defined as consisting of a infinite number of replicas of the given system under investigation.

8. Construction of an ensemble in the case of nonequilibrium

Now, let us consider the case of a nonequilibrium state. Recall that each nonequilibrium state is a transient one and the extent of inherent transientness depends on the fastness of the process that occurs. That is, the average time spent by a system in a nonequilibrium state would be far less than infinity. Indeed, for a very-very slow process, this number (the number of measurements of time intervals τ_{therm} which can be actually made) will be enormously large but as we go for more and more rapid processes this number goes on decreasing. That is, this number is directly proportional to the average lifetime of a given nonequilibrium state. In view of this, the corresponding ensembles will have less and less number of replicas of the system as the fastness of the processes that occur increases. In an extreme case, before a second measurement of time duration τ_{therm} can be made, the system has already drifted away from the said nonequilibrium state.

Thus, it is clear from the above discussion that one can still construct an ensemble for a given nonequilibrium state but the number of replicas of the system that would constitute an ensemble, will be less and less as the fastness of the involved process increases. But then the corresponding time average to be computed has to be for the relevant shorter time duration. Hence, with this understanding, the equivalence of the time averages of thermodynamic properties with its ensemble averages still holds. This way of computing (or measuring) a thermodynamic property does not bring in any significant contribution from the natural fluctuations to it because in doing so, $\overline{X}$'s have not been computed or measured for time intervals shorter than τ_{therm}. Thus, when the lifetime of a given nonequilibrium state is comparable to τ_{therm}, then the ensemble average consists of only a few replicas of the system making $\overline{X} \approx \overline{\overline{X}}$ while in other cases, we have $\overline{(\overline{X})} = \overline{\overline{X}}$. Again, the said restriction of the allowed shortest time duration equal to τ_{therm} is, in fact, an imposition of the dictates of the laws of thermodynamics on the measurements as well as on the statistical mechanical ensemble method of computing an average of a thermodynamic property.

The above revelations obviously are of fundamental importance for developing an irreversible thermodynamic framework. As far as the present author's knowledge goes, such an indepth consideration of the microscopic and macroscopic aspects of irreversible thermodynamics and nonequilibrium statistical mechanics have not been attempted in the literature. In our opinion, the conflicting assertions, the lack of confidence in comprehending the physical contents of the deductions and the blurredness that exists at various levels of description in the field of thermodynamics, have their roots in the lack of the above discussed required rigour in our understanding.

9. Concluding remarks

The aim of this paper was to clearly understand the 'universe of operations' of thermodynamics and what is the bearing of it at the macroscopic and microscopic levels of descriptions. This exercise revealed that the source of natural fluctuations is the non-operation of the 'equal *a priori* probability' of binary collisions and their reverse ones. This happens when the time interval of observations is less than τ_{therm}, the minimum time required for the sensing of thermal interaction, which in essence is the elaboration using the molecular level events of the dictate of the laws of thermodynamics. Thus, the methods appropriate for time intervals less than τ_{therm} are those of probabilistic in nature whereas for the time intervals equal to or greater than τ_{therm}, the probabilistic description culminates into the thermodynamic one [31]. Hence, an utmost care is required in identifying processes not falling within the purview of thermodynamics (irreversible). On the other hand, it is also required to carefully decide how far the Gibbsian ensemble method can be extended for developing a nonequilibrium statistical thermodynamics.

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[31] τ_{fluc} cannot be as short as the molecular collision duration. Hence, $\tau_{fluc} > 10^{-12} s$ and $\tau_{therm} = 10^{-11} - 10^{-9} s$ [20].